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Compositional modulation and long-range ordering in GaP/InP short-period superlattices grown by gas source molecular beam epitaxy

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Long-range ordering in a $(GaP)_2/(InP)_2$ short-period superlattice and a $Ga_{0.525}In_{0.475}P$ buffer layer grown on a (001)GaAs substrate by gas source molecular beam epitaxy were studied. Transmission electron microscopy and low-temperature cathodoluminesence techniques were used to examine the microstructure of the short-period superlattice and to determine its band-gap energy. The superlattice layer was found to have a [001] long-range ordered structure with a band gap narrowing of about 130 meV, while the $Ga_{0.525}In_{0.475}P$ layer had a 37 meV band-gap narrowing induced by spontaneous long-range ordering in the [111] direction. The ordered superlattice layer was found to have a growth-induced lateral periodic modulation of the composition along the [$\bar{1}$10] direction. Within the modulating bands, which had a 200 Å periodicity, the In composition was found to vary from 42 to 56% while the Ga correspondingly varied between 58 and 44%.

Spontaneous growth-induced ordering which lowers the band-gap energy by ~50 meV is typically observed in metalorganic chemical vapor deposition (MOCVD) grown $Ga_{0.5}In_{0.5}P$ epitaxial layers.[1] This type ordering has a CuPt-like structure, i.e., the column III sublattice, alternating (111)Ga and (111)In layers which grow in two of the four possible ⟨111⟩ directions.[2,3] Other compound semiconductors such as $Al_xGa_{1-x}As$, $Ga_{0.5}In_{0.5}As$, and $GaAs_{0.5}Sb_{0.5}$ tend to display a spontaneous CuAu-I type structure, i.e., ordering along the [001] direction.[4–6] While there are presently no reports describing the optical properties of spontaneously ordered CuAu-I structures, the optical properties of intentionally ordered CuAu-I structures have been investigated. In the $Al_xGa_{1-x}As$ material system, molecular beam epitaxy (MBE) grown $(AlAs)_n/(GaAs)_n$ short-period superlattice (SPS) structures were utilized to study this structure.[7,8] Employing low-temperature photoluminescence (PL), Isu *et al.*[8] observed that the amount of the band-gap narrowing was a function of the number of monolayers in each period of the SPS. The narrowing of the band gap was the greatest for $n=1$, smallest for $n=3$, and of some intermediate value for $n=2$ and $n=4$. In a study of $(GaAs)_n/(InAs)_n$ SPS grown on InP by MOCVD, Fukui and Saito[9] also found that the apparent band-gap narrowing increased for n between 0.7 and 1.3. Due to the 7% lattice mismatch between the GaAs and InAs, the crystal quality of the SPS degraded for n nearing 2, and no low-temperature (77 K) PL was detected. In this letter, in spite of the even larger lattice mismatch of 8% between GaP and InP, we report the growth of $(GaP)_2/(InP)_2$ SPS on a (100)GaAs substrate. The microstructure of the SPS was characterized by transmission electron microscopy (TEM), and the ordering related band-gap narrowing properties for both as-grown and annealed materials were studied with low-temperature cathodoluminescence (CL).

The growth of $(GaP)_2/(InP)_2$ SPS was performed on an n-type (100)GaAs substrate by gas source molecular beam epitaxy (GSMBE) using elemental Ga and In, and P_2 cracked from PH_3 as the source materials. Details of the growth system and characteristics of the hydride cracker have been reported elsewhere.[10] With the growth temperature at 510 °C, a 0.47 μm undoped $Ga_xIn_{1-x}P$ buffer layer with a lattice constant close to that of GaAs was first grown on the substrate. This was followed by the growth of an undoped 110-period $(GaP)_2/(InP)_2$ SPS layer. Reflection high-energy electron diffraction intensity oscillations were used to calibrate the growth rate so that each layer could be grown two monolayers thick. Double-crystal x-ray diffractometry (DCXD) was used to determine the lattice constant and corresponding composition of the $Ga_xIn_{1-x}P$ buffer layer. The value of x was found to be 0.525.

The structure of the $(GaP)_2/(InP)_2$ SPS was further examined by cross-sectional TEM. Figure 1 shows the electron diffraction patterns for the SPS in two perpendicular ⟨110⟩ directions. Satellite reflections are clearly seen around the fundamental reflections along the [002] growth direction. The distance between the satellite spot and the nearest neighboring fundamental spot is approximately 1/4 the distance separating two neighboring fundamental [002] reflections. This is an indication that the period of SPS is roughly four monolayers. It is also noteworthy that the shapes of the 1/4 [002] diffraction spots are different for both ⟨110⟩ directions. In the [$\bar{1}$10] cross section they appear round and symmetric, while in the [110] cross section they appear elongated. Such differences indicate a loss of symmetry between morphologies of the [110] and [$\bar{1}$10] cross sections of the superlattice layer, as can be clearly seen in Fig. 2. A uniform image appears in the [$\bar{1}$10] cross section using (002) dark field imaging, while weak modulating dark and white bands, approximately 100 Å wide and parallel to the growth direction are clearly visible in the view of the [110] cross section. Energy dispersive x-ray microanalysis performed with a 10 Å electron beam probe

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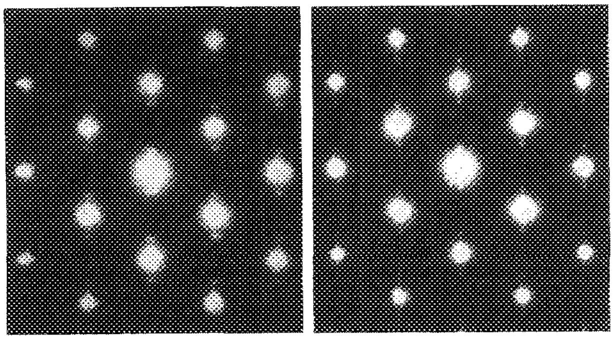


[110] [$\bar{1}$10]

FIG. 1. Selected area transmission diffraction patterns of the $(GaP)_2/(InP)_2$ short-period superlattice in both [110] and [$\bar{1}$10] cross sections. The shapes of the 1/4 [002] satellite diffraction spots are different for both ⟨110⟩ directions.

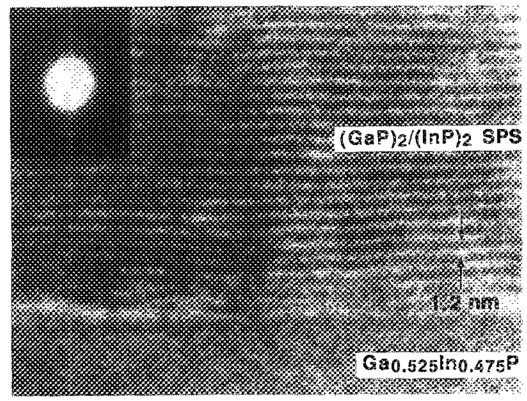
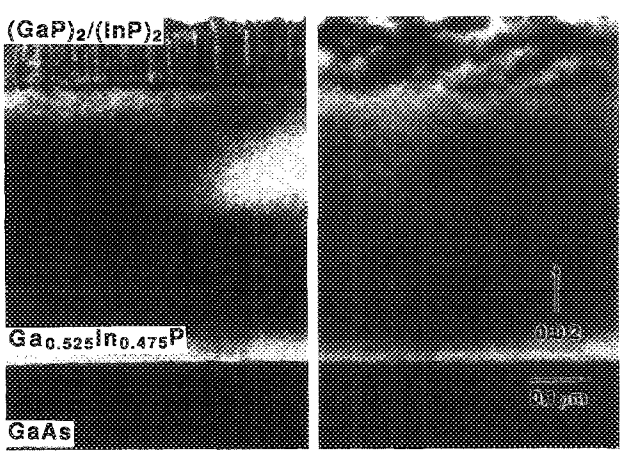


FIG. 3. Bright field cross-sectional transmission electron micrograph of the $(GaP)_2/(InP)_2$ short-period superlattice grown on the $Ga_{0.525}In_{0.475}P$ buffer layer. The image was formed from the transmitted beam and two adjacent superlattice reflections as shown in the inset.

reveals that the dark and white bands are actually a relative variation of the column III composition. A higher than average In content was found to exist within the white bands while a higher than average Ga content within the dark bands. A maximum composition of $Ga_{0.44}In_{0.56}P$ was measured for the In-rich bands and $Ga_{0.58}In_{0.42}P$ for the Ga-rich bands. This growth-induced modulation of the composition was found to be plate-like with each plate nearly parallel to [110] direction. Because of the nature of the plate-like structure, streaking is expected to appear around each electron diffraction spot in the direction normal to the plate. As expected, this electron diffraction pattern was found around the superlattice reflections in the [110] zone-axis. To further study the composition modulation phenomenon, a [110] cross-sectional bright field TEM micrograph of a sample imaged with the transmitted beam and two adjacent superlattice reflections was recorded as is shown in Fig. 3. We note that the superlattice fringes with spacings of 12 Å appear flat and smooth near the buffer layer interface and show corrugations near the surface. The spacing is slightly larger than 11.3 Å which would be expected of a SPS formed by two monolayers of GaP and two monolayers of InP. This indicates that the deposition rate of Ga and/or the In atoms deviated from exactly two monolayers. As a result, while most of the growth surface has a $(GaP)_2/(InP)_2$ SPS structure, some areas contain more than two monolayers of GaP or InP. Due to the 8% lattice mismatch between GaP and InP, the excess column III atoms will rearranged themselves in order to minimize the total free energy. Consequently, a growth-induced lateral periodic variation in the composition along the [$\bar{1}$10] direction was formed in the SPS structure. The mechanism responsible for the formation and the reason for the directional dependency of the plate-like structure are unclear at the present time, but it is the subject of further study. Its origin is not believed to be attributable to instabilities in the source flux or substrate temperature, however, as this usually results in strain relaxation which is perpendicular to the growth direction.[11]



[110] [$\bar{1}$10]

FIG. 2. Dark field cross-sectional transmission electron micrographs of the $(GaP)_2/(InP)_2$ short-period superlattice grown on the $Ga_{0.525}In_{0.475}P$ buffer layer along the [110] and [$\bar{1}$10] cross sections. Note that within the SPS layer a uniform image appears in the [$\bar{1}$10] cross section while weak white and dark bands are observable in the [110] cross section.

Low-temperature (~90 K) CL having an electron energy of 20 keV was performed on the sample cross section to determine the band gaps of the epitaxial layers. Since the $(GaP)_2/(InP)_2$ SPS has an average composition that is close to that of the buffer layer, their corresponding peak emission energies should be near one another. Instead, as shown in curve (a) of Fig. 4, in addition to the $Ga_{0.525}In_{0.475}P$ layer emission peak at 6263 Å, a second peak at 6795 Å is observable in the as-grown sample. This energy is ~150 meV lower than a correspondingly unordered bulk $Ga_{0.5}In_{0.5}P$ layer. Since both SPS and buffer layer are undoped and the relative emission intensity of the CL spectra at 6795 Å is strong, it cannot be attributed to any donor/acceptor transition. One possible explanation for the large disparity is ordering induced band-gap narrowing, similar to the $(AlAs)_n/(GaAs)_n$ and $(GaAs)_n/(InAs)_n$ SPS previously studied.[8,9] In order to more precisely quantify the band-gap narrowing effect, the SPS structure was disordered by annealing at 825 °C for 5.5 h in a sealed ampoule under a P_4 atmosphere. As shown in

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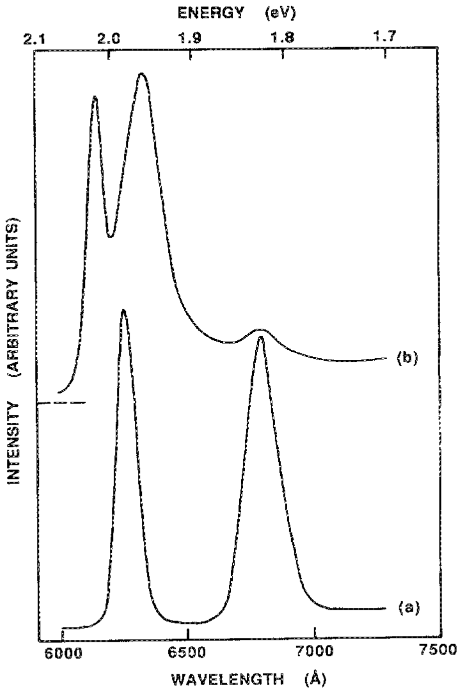

FIG. 4. Low-temperature (~90 K) cathodoluminescence spectra of the: (a) as-grown and (b) annealed $(GaP)_2/(InP)_2$ short-period superlattice and $Ga_{0.525}In_{0.475}P$ buffer layer.

curve (b) of Fig. 4, three peaks are clearly seen in the low-temperature CL spectra of the disordered material. The least intense peak at ~6790 Å indicates that there are regions within the annealed SPS structure which have retained the CuAu-I type ordering and therefore, have an emission energy like that of the as-grown SPS. The peak at 6148 Å corresponds to the band-gap energy of the disordered $Ga_{0.525}In_{0.475}P$ buffer layer and it is 37 meV higher than that of the as-grown layer. The electron diffraction pattern for the as-grown buffer layer in the [110] direction originally showed the existence of very weak additional 1/2 ⟨111⟩ reflections typical of CuPt-type ordering. This weakly ordered structure is often observed in our $Ga_xIn_{1-x}P$ samples grown on GaAs. Room-temperature PL measurements performed on separate bulk $Ga_xIn_{1-x}P$ samples show a typical band-gap narrowing of 25 meV.[12] These results are consistent with those observed for $Ga_{0.5}In_{0.5}P$ grown either above 750 °C or below 550 °C by MOCVD, and which also show very weak 1/2 ⟨111⟩ reflections in the electron diffraction pattern and exhibit a band-gap narrowing of less than 30 meV.[13] The third peak at 6335 Å is due to the disordered regions within the SPS after heat treatment and it is 130 meV higher than that of the as-grown SPS layer. When CuPt-type ordered structures are disordered either by thermal annealing or through impurity-induced disordering, the In and Ga atoms become randomized and subsequently the emission energy approaches that of a bulk homogeneous layer. The emission from the disordered SPS region indicates that the average composition of the as-grown SPS layer is approximately $Ga_{0.485}In_{0.515}P$, which is very close to that of a $(GaP)_2/(InP)_2$ SPS.

Recently, the stability of ordered phases in isovalent compound semiconductors was theoretically modeled using a self-consistent total energy calculation.[14] This model predicts that at low growth temperatures ordered phases in alloys with a large lattice mismatch e.g., GaAs/InAs and GaP/InP, are more stable than disordered phases. A 40 meV lowering of the band-gap energy was calculated for CuAu-like long-range [001] ordering in $(GaAs)_1/(InAs)_1$ and 70 meV in $(GaP)_1/(InP)_1$. While the predicted 40 meV energy shift for $Ga_{0.5}In_{0.5}As$ was found to be consistent with experimental observation,[9] the one monolayer $Ga_{0.5}In_{0.5}P$ structure has yet to be constructed.

In conclusion, a $(GaP)_2/(InP)_2$ SPS and a $Ga_{0.525}In_{0.475}P$ buffer layer were grown on a (100)GaAs substrate by GSMBE. In addition to the 12 Å periodicity along the growth direction, the SPS also had a lateral 200 Å periodic variation in composition along the $[\bar{1}10]$ direction. Across the modulating bands, the In content varied between 42 and 56% while the Ga varied correspondingly between 58 and 44%. The photon emission energies obtained from the low-temperature CL spectra of the as-grown and annealed samples indicate a band-gap narrowing of greater than 130 meV for the SPS layer. The $Ga_{0.525}In_{0.475}P$ buffer layer had a 37 meV band-gap narrowing and it is attributed to a weak CuPt-type ordering.

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